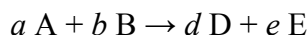


## INTRODUCTION TO KINETICS POGIL

### Reaction Rates

Chemical kinetics is the part of chemistry that looks at how fast reactants are converted into products in order to establish an experimental rate law, which can be used to decide how the reaction occurs. Knowing the reaction mechanism, the series of steps by which each reaction occurs, and the factors that affect the rate of a reaction makes it possible for the chemist to plan the efficient and cost effective production of industrial, pharmaceutical, and consumer chemicals. You will find that understanding reaction rates is essential to understanding how reactions occur.

Suppose we are interested in the generic chemical reaction as a way to synthesize the product D:



If we wish to synthesize D and sell it commercially, it would be undesirable if too little of it is produced by the time we want to sell it. And (for example, if the reaction is exothermic) it would be unacceptable and perhaps dangerous for too much D to be produced per unit of time. Hence, it is necessary that we can determine and control the rate at which D is produced in the reaction vessel.

If the volume of the reaction mixture is a constant, we can define the rate of reaction as:

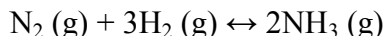
$$Rate = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

where  $\Delta[D]$  is how much the molar concentration of D changed in the amount of time that passed,  $\Delta t$  and  $d$  is the stoichiometric coefficient of D. It may be more convenient to monitor the reaction rate in terms of how the concentration of A (or the concentration of another species in the reaction mixture) is changing with time. In that case:

$$Rate = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} = \frac{1}{e} \frac{\Delta[E]}{\Delta t}$$

- 1) The rate for the generic reaction above can be expressed in several different but equivalent ways. When the rate is expressed in terms of the rate of change of the concentration of A or B (e.g.  $-\Delta[A]/\Delta t$ ), the expression is written with a negative sign, but when the rate is expressed in terms of the concentration of D or E it is expressed with a positive sign (e.g.  $\Delta[D]/\Delta t$ ). Explain why.

- 2) As a specific example, consider the consumption of nitrogen and hydrogen gases to produce gas:



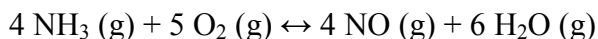
Fill in the blanks with the appropriate numbers and signs to describe the rate of the reaction in terms of each reactant and/or product.

(a) \_\_\_\_\_  $\frac{\Delta[\text{N}_2]}{\Delta t} =$  \_\_\_\_\_  $\frac{\Delta[\text{H}_2]}{\Delta t}$

(b) \_\_\_\_\_  $\frac{\Delta[\text{N}_2]}{\Delta t} =$  \_\_\_\_\_  $\frac{\Delta[\text{NH}_3]}{\Delta t}$

### Model #1

The reaction between ammonia and oxygen at the temperature of the reaction vessel is:



Initially at some temperature, the only substance present in a 10.0 L reaction vessel is 50.0 mol of  $\text{NH}_3$  gas. An excess of  $\text{O}_2$  gas is quickly pumped into the reaction vessel without changing either the vessel's volume or the system's temperature. After 10.0 seconds time, there are only 26.0 mol of  $\text{NH}_3$  remaining. (There is still some left over  $\text{O}_2$ , and the reaction is still proceeding.)

- 3) (a) What is the initial molar concentration of  $\text{NH}_3$ ?
- (b) What is the final molar concentration of  $\text{NH}_3$ ?
- (c) What is the change in the molar concentration of  $\text{NH}_3$  ( $\Delta\text{NH}_3$ )?
- (d) What is the change in time ( $\Delta t$ )?
- (e) What is the rate of change of the molar concentration of  $\text{NH}_3$ ?

$$\text{Rate} = \frac{\Delta[\text{NH}_3]}{\Delta t} =$$

- 4) Use your answer from question #3 to determine the rate of change of the concentrations of  $O_2$ , of  $NO$ , and of  $H_2O$ . First fill in the appropriate relationships between the rate of  $NH_3$  and each of the other reactant and/or products. Then using that relationship, determine the rate for each reactant and/or product.

$$Rate = \frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

$$\frac{\Delta[O_2]}{\Delta t} =$$

$$Rate = \frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[NO]}{\Delta t}$$

$$\frac{\Delta[NO]}{\Delta t} =$$

$$Rate = \frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[H_2O]}{\Delta t}$$

$$\frac{\Delta[H_2O]}{\Delta t} =$$

### *Factors Affecting Reaction Rates*

There are multiple aspects that affect the rate of a reaction: concentrations of reactants and/or products, surface area of reactants, temperature, and catalysts (which we will talk more about later). However, before looking at how these factors affect the reaction rate, we need to discuss what happens on a molecular level in a reaction, which is described by the collision theory.

The collision theory states that a chemical reaction can only occur between particles when they collide (hit each other). The collision between reactant particles is necessary but not sufficient for a reaction to take place. The collisions also have to be effective. It is important to understand the exact nature of an effective collision since this determines whether or not particles actually react with each other and form new products.

### Model #2

In the picture to the right, the baseball bat represents Reactant A and the baseball represents Reactant B. A reaction will only be successful if the batter hits a homerun. If the batter does not hit a homerun, the reaction will be considered a failure.

- Scenario 1: The pitcher throws a fastball down the middle of the



plate. The batter takes a mighty swing and totally misses the ball. The umpire yells, "Strike one!"

- Scenario 2: The pitcher throws an off-speed pitch and the batter checks his swing. The batter just barely makes contact with the ball and it dribbles down in front of the batter's feet into foul territory. The umpire yells, "Foul ball; strike two!"
- Scenario 3: The pitcher throws a curve ball that looks like it might catch the outside corner of the plate. The batter swings with all his strength, but the bat grazes the underside of the ball and the ball skews off to the right, flying into the crowd. The umpire yells, "Foul ball, still two strikes!"
- Scenario 4: The pitcher throws another fastball down the middle of the plate. The batter swings and wallops the ball high into the air and the ball clears the center field wall that reads 410 feet. The ump yells, "Homerun!"

1) For each of the above situations, decide if there is a reaction occurring. Explain why or why not.

(a) Situation 1

(b) Situation 2

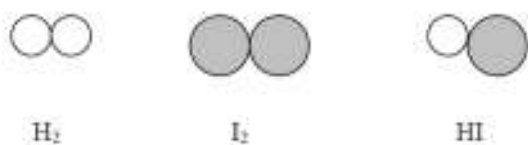
(c) Situation 3

(d) Situation 4

2) (a) What two aspects allows for effective collision?

(b) Finish the following statement: Collision theory states a reaction is most likely to occur if...

- 3) Hydrogen gas and iodine vapor combine to form hydrogen iodide gas, as shown in the equation  $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$ . Using the representations shown below, draw a diagram to show an orientation for the reactant molecules that could produce an effective collision capable of producing two hydrogen iodide molecules.



Now that you understand how reactions occur on a molecular level, let's discuss how each of the different factors affects the rate of a reaction. Increasing the concentrations of reactants increases the chances for more molecular collisions which make products. Usually the increase in concentrations of the reactants will increase the rate of a reaction. Increasing the surface area of the reactants will also increase the number of collisions. Increasing the temperature of a reaction will also speed it up. Increasing the temperature increases the rate of both forward and reverse reactions, increasing the number of collisions over a period of time.

### Model #3

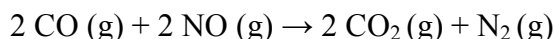
- Calcium carbonate and hydrochloric acid

In the lab, powdered calcium carbonate reacts much faster with dilute hydrochloric acid than if the same mass was present as lumps of marble or limestone. The reaction below occurs faster with concentrated hydrochloric acid than with dilute HCl.



- Catalytic converters

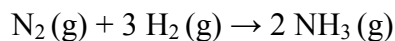
Catalytic converters use metals like platinum, palladium and rhodium to convert poisonous compounds in vehicle exhausts into less harmful things. For example, a reaction which removes both carbon monoxide and an oxide of nitrogen is:



Because the exhaust gases are only in contact with the catalyst for a very short time, the reactions have to be very fast. The extremely expensive metals used as the catalyst are coated as a very thin layer onto a ceramic honeycomb structure to maximize the surface area.

- The manufacture of ammonia

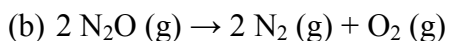
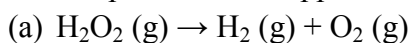
The rate of reaction between the hydrogen and the nitrogen is increased by the use of very high pressures.



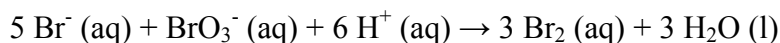
- 4) For each example above, explain how the rate is changed, based on the information above. Consider what is happening on a molecular level in each reaction.

### *Problems*

- 1) For each of the following reactions, write the rate expression in terms of the appearance of each product or disappearance of each reactant:



- 2) For the reaction



it was found that a particular instant bromine was being formed at a rate of 0.039 mol/L·s. At that instant, at what is

- (a) water being formed?
- (b) bromide ion being oxidized?
- (c)  $\text{H}^+$  being consumed?

- 3) Nitrosyl chloride (NOCl) decomposes to nitrogen oxide and chlorine gases.
- (a) Write a balanced equation for the decomposition.
  
  - (b) Write an expression for the reaction rate in terms of  $\Delta[\text{NOCl}]$ .
  
  - (c) The concentration of NOCl drops from 0.580 M to 0.238 M in 8.00 min. Calculate the average rate of reaction over this time interval.

\*Adapted from "ALE 1. Chemical Kinetics: Rates of Chemical Reactions" by Ken Marr (<http://www.instruction.greenriver.edu/kmarr/Chem%20163/Chem%20163%20ALEs.htm>) and "Collision Theory" by Stony Brook University, 2006.